Analytical Method for Measuring Total Protium and Total Deuterium in a Gas Mixture Containing H_2, D_2, and HD via Gas Chromatography

H. T. Sessions Jr.

Savannah River National Laboratory: Aiken, SC 29808, Henry.Sessions@SRNL.DOE.GOV

A new analytical technique for measuring both total protium and total deuterium in a gas mixture containing H_2, D_2, and HD has been developed.

I. INTRODUCTION

The most common analytical method of identifying and quantifying non-radioactive isotopic species of hydrogen is mass spectrometry. A low mass, high resolution mass spectrometer with adequate sensitivity and stability to identify and quantify hydrogen isotopes in the low ppm range is an expensive, complex instrument.

A new analytical technique has been developed that measures both total protium (H) and total deuterium (D) in a gas mixture containing H_2, D_2, and HD using an inexpensive micro gas chromatograph (GC) with two molecular sieve columns. One column uses D_2 as the carrier gas and the other uses H_2 as the carrier gas. Laboratory tests have shown that when used in this configuration the GC can measure both total protium and total deuterium each with a detection and quantification limit of less than 20 ppm.

II. BACKGROUND

This new analytical technique was developed as a result of a request from the Tritium Facility Modernization and Consolidation (TFM&C) project at the Savannah River Site (SRS) to provide instrumentation to measure the protium and deuterium concentrations at several process points during initial testing of new Hydrogen Tritium Thermal Cycling Absorption Process (HT-TCAP) columns

The purpose of a HT-TCAP system is to separate tritium from other hydrogen isotopes and minimize environmental releases of tritium. A new HT-TCAP system was installed to primarily separate protium and tritium from Z-Bed Recovery gases. Prior to introducing tritium into this new HT-TCAP system, TFM&C decided to test the system by substituting non-radioactive deuterium mixtures for tritium mixtures. Two of the major process points of interest were the column raffinate and the column product.

During normal tritium operations, after several thermal process cycles, the column raffinate will contain high purity protium, which may be released to the atmosphere via the stack, and the column product will contain high purity tritium, which is transferred to hydride beds for storage. The limit for environmental releases of column raffinate is less than 5 atom ppm of tritium as HT, DT, or T_2. The column product quality for tritium is less than 0.1 atom % protium as HT, HH, or HD.

The instrument of choice to monitor the HT-TCAP process during normal tritium operation is an ion chamber. It is relatively inexpensive, simple to operate, and has sensitivity equivalent to less than 1 ppm. Theoretically an ion chamber can detect the decay of one tritium atom. Therefore, monitoring for small quantities of tritium in the raffinate is relatively simple.

However, for start-up test purposes, D_2 was substituted for T_2 and monitoring the column raffinate for small amounts of D_2 in pure H_2 presents a significant analytical challenge. Also, monitoring the column product for small amounts of H_2 in pure D_2 is a significant analytical challenge. To further complicate matters the HT-TCAP will also produce HD which may be in either the raffinate or product. Therefore, the analytical challenge for the test was to provide instrumentation to measure both total D in the column raffinate, and total H in the column product.

III. Initial Instrumentation and HT-TCAP Testing

A Residual Gas Analyzer (RGA), a Gas Chromatograph (GC), and a Helium Leak Detector were the instruments chosen to monitor the HT-TCAP process during initial field testing. Each instrument has unique capabilities and limitations which will not be elaborated on in this report.

Used in conjunction, although cumbersome, these three instruments can trend the operation of the HT-TCAP process and demonstrate that it separates protium and

deuterium. The instrumentation will show a decreasing concentration of deuterium in the column raffinate and an increasing concentration of deuterium in the column product. Final determination of HT-TCAP performance is accomplished by obtaining grab samples from the column raffinate and column product and analyzing them using a low mass high resolution mass spectrometer. It was the need for a singular instrument to monitor the HT-TCAP performance that lead to the development of the new analytical method using a GC.

IV. Development of New Analytical Method

The typical configuration of a GC to detect H_2 is a molecular sieve column with argon carrier gas and a thermal conductivity detector. The limitation of this configuration for testing the HT-TCAP process is the inability of the molecular sieve column to separate the hydrogen isotopes. (H_2, D_2, and HD). All of these species co-elute which makes it impossible, with a thermal conductivity detector, to identify and quantify each isotope. To solve this problem the author conjectured that changing from argon carrier to H_2 carrier would allow the GC to mask the signal contribution of H_2, (in a sample containing both $H_2$and D_2) and leave only the deuterium signal. Additionally, if D_2 were used as the carrier gas, it would mask the signal contribution of D_2 (in a sample containing both H_2 and D_2), and leave only the hydrogen signal. What was unknown was how this GC configuration would respond to the presence of HD in the sample mix.

The GC used for testing the HT-TCAP process and subsequently to develop this new analytical technique is a model M200 originally manufactured by Microsensor Technology Inc. and now manufactured by Agilent. This model GC has been applied to numerous processes and experimental work at SRS. It can be configured with two columns and two different carrier gases, which made it well suited for testing and developing this new analytical technique. Samples injected into the GC are analyzed simultaneously by the two columns. Analysis time is approximately 45 seconds.

A model M200 GC was configured with two molecular sieve columns. One column supplied with H_2 carrier gas and the other column supplied with D_2 carrier. Both columns were equipped with thermal conductivity detectors.

Initially gas mixtures containing (25% H_2, 75% D_2), (50% H_2, 50% D_2), and (75% H_2, 25% D_2 were analyzed. As anticipated each GC column displayed only one peak and this peak amplitude varied as predicted. The maximum height of the peak for the GC column with H_2 carrier gas was with the (25% H_2, 75% D_2) mixture and the minimum peak height was produced by (75% H_2, 25% D_2) mixture. This data meant that the peak represented D_2 concentration. The maximum height of the peak for the GC column with D_2 carrier gas was produced by the (75% H_2, 25% D_2) mixture and the minimum peak height was with the (25% H_2, 75% D_2) mixture. This data meant that the peak represented H_2 concentration. A three point calibration curve was generated for each GC column based on the area under the curve for each analysis.

Next, a test was performed with a mixture containing H_2, HD, and D_2) to determine how each column would respond to the presence of HD. (HD was generated by passing a 50% mixture of H_2 and D_2 through a palladium silver diffuser.) The results showed that the GC column with deuterium carrier gas measured a value of approximately 50% H_2 and the GC column with hydrogen carrier gas measured a value of approximately 50% D_2. In essence this GC configuration gave a measurement of the total amount of deuterium and the total amount of protium in the sample mixture. Various other mixes of (H_2, HD, D_2) were analyzed and each time values of total deuterium and total protium were correctly quantified. The sensitivity to both protium and deuterium was determined to be less than 20 ppm. This is significantly better sensitivity than the high resolution mass spectrometers at SRS which have a detection limit of 100 ppm for H_2 and D_2.

V. Test Data Using New Analytical Method

Enumerated and tabulated below are the test sequences and data from the development of this method.

1) The following partial pressure gas mixtures were made for use as calibration gases

   50% H_2 50% D_2
   75% D_2 25% H_2
   25% H_2 75% D_2

2) These gas mixtures were analyzed by the GC. The table below shows the analytical results. Each gas sample was analyzed three times.

GC Analysis Of H_2 D_2 Mixtures					
		Analysis # 1	**Analysis # 2**	**Analysis # 3**	**Average**
Mixture 50% D_2 50% H_2		(Area Counts Under Curve)			
Column A (H2 carrier Gas)	D_2=	69,140,528	69,140,658	69,149,321	**69,143,502**
Column B (D2 Carrier Gas)	H_2=	48,541,600	48,541,455	48,545,632	**48,542,896**
Mixture 75% D2 25% H2					
Column A (H_2 carrier Gas)	D_2=	100,414,040	100,464,512	100,593,056	**100,490,536**
Column B (D_2 Carrier Gas)	H_2=	24,483,564	24,507,014	24,551,368	**24,513,982**
Mixture 25% D2 75% H2					
Column A (H_2 carrier Gas)	D_2=	36,488,572	36,493,176	36,531,768	**36,504,505**
Column B (D_2 Carrier Gas)	H_2=	71,972,384	72,009,008	72,042,288	**72,007,893**

3) A calibration curve was generated for each column based on the area under each peak from each analysis.

$\%D_2 = 7.813E\text{-}07*X - 3.69$ X = Area Counts
$\%H_2 = 1.053E\text{-}06*X - 0.904$ X = Area Counts

4) The gas mixtures listed in step one were passed through a palladium diffuser to generate the following mixtures containing HD. These mixtures were also analyzed by the a high resolution mass spectrometer to provide a traceable analysis.

Diffuser Input 25%D_2 75%H_2	H_2	HD	D_2
Mass Spec Analysis of Output	56.67%	36.69%	6.64%
Diffuser Input 75%D_2 25%H_2	H_2	HD	D_2
Mass Spec Analysis of Output	6.82%	36.97%	56.22%
Diffuser Input 50%D_2 50%H_2	H_2	HD	D_2
Mass Spec Analysis of Output	26.36%	48.73%	24.89%

5) The gas mixtures containing HD were analyzed by the GC. The table below shows the analytical results.

GC Analysis of Diffuser Output	
Mixture Analyzed	GC Analysis
H_2 (26.36%), HD (48.73%), D_2 (24.89%)	
Column A (D_2 carrier Gas)	H_2=51.36%
Column B (H_2 Carrier Gas)	D_2=48.51%
Mixture Analyzed	
H_2 (6.82%), HD (36.97%), D_2 (56.22%)	
Column A (D_2 carrier Gas)	H_2=26.12%
Column B (H_2 Carrier Gas)	D_2=73.70%
Mixture Analyzed	
H_2 (56.67%), HD (36.69%), D_2 (6.64%)	
Column A (D_2 carrier Gas)	H_2=75.87%
Column B (H_2 Carrier Gas)	D_2=23.94%

6) ½ of the HD value from the Mass Spec Analysis was added to either the H_2 or D_2 value. These calculated values were then compared to the GC analysis.

Mass Spec Analysis	1/2 HD + (D2 or H2)	GC Analysis
D2=24.89%		
H2=26.36%	1/2 HD+D2 = 49.25%	D2=48.51%
HD=48.73%	1/2 HD+H2 = 50.72%	H2=51.36%
D2=56.22%		
H2=6.82%	1/2 HD+D2 = 74.70%	D2=73.70%
HD=36.975%	1/2 HD+H2 = 25.30%	H2=26.12%
D2=6.64%		
H2=56.67%	1/2 HD+D2 = 24.99%	D2=23.94%
HD=36.69%	1/2 HD+H2 = 75.01%	H2=75.87%

7) To determine the limit of detection of this analytical technique for D_2, the gas mixture containing 6.82% H_2, 56.22% D_2, and 36.97%HD was incrementally diluted with H_2 and measured with the GC.

Test Data to Determine Limit of Detection		
Dilution	Theroretical Values PPM	GC Analysis PPM
0	747,000	734,910
10	74,643	74,980
100	7,464	7,658
1001.0	746.4	776.5
10009.6	74.6	78.4
20038.0	37.3	39.8
40722.0	18.4	19.4
81688.2	9.2	8.2

VI. Conclusions

A micro GC configured with two molecular sieve columns and separate carrier gases (one H_2 the other D_2) provides a low cost, fast means of quantifying total protium and total deuterium in a gas mixture containing H_2, D_2 and HD. Detection and quantification of protium or deuterium using this technique is at least 20 ppm. Samples containing tritium have not been analyzed with this method. Results of such analysis would be of great interest and could possibly lead to a simple analytical method for tritium.

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